BOUTIN, PRASK and TREVINO

STUDY OF LOW FREQUENCY MOLECULAR MOTIONS IN EXPLOSIVES BY SLOW NEUTRON INELASTIC SCATTERING

HENRI P. BOUTIN, HENRY J. PRASK and SAMUEL TREVINO
Explosives Laboratory, Picatinny Arsenal
Dover, New Jersey

JUL 6 1966

Experimentally, the investigation of reactions in explosive materials has, until fairly recently, been concerned largely with fast reactions. There are obvious difficulties inherent in these experiments due to the very short time in which processes occur, the complication of mass flow (that is massive transport of material as, for example, in the region of a shock or pressure wave) and the inability to determine the thermodynamic parameters due to extreme temperatures and pressures. These experiments have, however, led to good phenomenological descriptions of the propagation of detonation. However, they have yielded little insight into the mechanism of growth of reaction, particularly in regard to the nature of reaction at the molecular level. A knowledge of the conditions necessary for initiation of detonation is of great practical importance both from the viewpoint of causing a detonation to occur when it is desired and also to prevent it from occurring when it is not. This problem has received considerable study and many methods have been designed for its achievement. However, since the detailed mechanism of initiation at the molecular level is unknown, this exact control of initiation is not presently attainable.

It seems likely that the stimulus responsible for the subsequent release of chemical energy is primarily thermal and that other practical means of producing initiation (the application of shock, mechanical action, electrostatic charge, sparks and high intensity light pulses) are probably thermal in their effect. An investigation was therefore undertaken of the thermal reactions in solids which may subsequently grow into deflagration or detonation. Scientifically initiation is an indeterminate property, however, it includes the point in time at which the growth reactions become apparent. These growth reactions can be classified into three general kinds:

a. The first involves "chains" of reactions within the bulk of the solid or at the surface of the solid, the chain being

propagated by either products of the reactions (atoms in new charge states, charge carriers themselves, or electronic excitation) or vibrational excitation, where the energy released by individual steps in the process may be considered to be contributing to local changes in temperatures ("hot spot" model).[3]

b. The second type deals with processes within the material leading to products which are transported to sites on the surface or at grain boundaries and the like. The products would be then considered to aggregate to form new unstable phases.

c. The third category considers the possibility of a direct phase change of the material accompanied by a release of energy, the material having become vibrationally unstable. This latter type of model differs importantly from the first two classes in that no transport of reaction products is involved. Although this mechanism does not account for the known effect of relatively small quantities of impurities and the apparent importance of surface reactions in explosives, a relatively large number of phase changes have been observed in explosive materials and the possibility of a large energy release after a phase change is of interest.

In the study of these various models of growth reactions, the technique of neutron scattering can provide information which is essential to the understanding of the processes taking place at the molecular level. These processes involve both intra- and inter-molecular vibrations of the molecular arrangement and their changes at different stages of the reaction. The third mechanism could be investigated by noting, for example, that lattice vibrational modes must show the onset of a phase change. The results of thermal decomposition or irradiation experiments or the known effects of imperfections (dislocations, defects or impurities) on the explosive sensitivity can now be investigated on the microscopic level. An attempt to correlate these findings with the microscopic properties of explosive or related materials may therefore become possible.

This paper reports the preliminary results of these studies. First, we shall describe the ways in which neutrons may interact with nuclei in a solid or liquid and the various types of information which can be obtained from these measurements.

Neutron diffraction is now used quite extensively, often as a necessary complement of x-rays, to determine the position of light atoms (especially hydrogen) in a crystalline structure. Neutrons of thermal energy (kT=25 millielectron volts) are scattered elastically (without exchanging energy) and the neutron waves scattered from the periodically arranged nuclei give rise to interference effects or Bragg reflection. We obtain, in this case, a "static" picture of the crystal, that is, every atom is vibrating around its equilibrium position. Neutrons can also be used as "probes" to study the dynamics of motions of atoms and molecules in the crystal. If their incident energy is small (5 mev) compared to the vibrational energy of the atom in the crystal (kT=25 mev), energy will be gained by these

neutrons in a scattering event and an analysis of the distribution in energy of these neutrons after scattering will reflect the dynamics of motion inside the crystal. Those motions are observed which take place in the far infrared frequency region (from 40 to 800 cm^{-1}) without being subject to symmetry dependant selection rules, so that all possible transitions are observable. Although the energy resolution is not, as yet, comparable to optical spectroscopic methods, the technique of neutron inelastic scattering offers a complement to Infrared or Raman techniques. It should also be noted that this technique is most sensitive to the motions of hydrogen atoms since the scattering cross-section for hydrogen is considerably larger ($\sim$ 80 barns) than for any other atom. In the case of monatomic solids with cubic symmetry, the frequency distribution, $g(\nu)$, (i.e., the number of states occurring per unit frequency interval) can be obtained exactly from the measured neutron differential inelastic scattering cross-section. Only approximate values of $g(\nu)$ can be obtained in the case of polyatomic molecules with a symmetry other than cubic. From the frequency distribution fundamental macroscopic properties such as specific heat (C_v), entropy (S), internal energy (E) and free energy (F) can be derived.

In this work, vibrational frequencies in the far infrared region (30-1000 cm^{-1}) which have not been obtained previously or are optically inactive will be presented for β and γ HMX, RDX, picric acid and lead styphnate. This frequency region is of importance since it is expected to contain most lattice modes (inter-molecular vibrations) and also because the low intra-molecular frequencies are more sensitive than the higher frequency vibrations to impurities in the lattice or to change in molecular conformation. The derived frequency distribution will be used to calculate thermodynamic quantities and to compare them with measured values where available.

$\underline{\beta}$ and $\underline{\gamma}$ HMX and RDX: These nitramine compounds are secondary explosives with comparable sensitivity. RDX forms a six membered ring, whereas HMX forms an eight membered ring and can exist in several polymorphic forms (α, β, γ, δ). Of the two forms which have been studied in this work, β HMX forms the more compact structure, the γ form being more open.
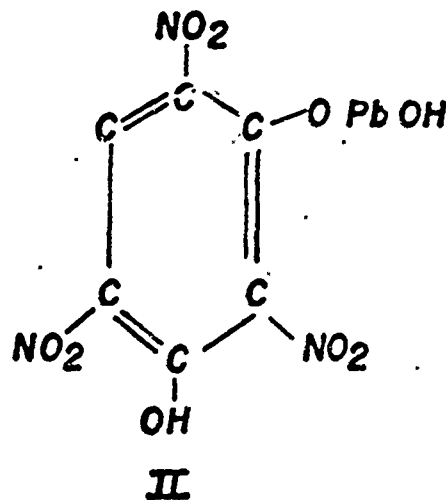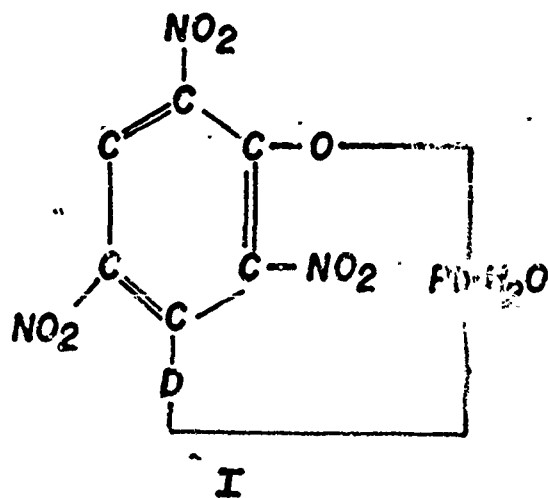
The spectra of scattered neutrons for these three explosives are shown in Figures 1 and 2. Table 1 gives a summary of the inelastic neutron scattering results for RDX and HMX and tentative assignments of the vibrational frequencies together with available infrared data of these compounds in the frequency range below 1200 cm^{-1}. The similarity of the vibrational frequencies in these compounds is not unexpected since they have the same chemical groups and comparable bond distances and bond angles. It should be noted that in the case of β and γHMX, the neutron spectra show differences in shape, especially in the region of lattice modes (an additional peak at 105 cm^{-1} is observed in β HMX). These spectral differences show the sensitivity of the neutron scattering technique to conformational changes and differences in intermolecular crystalline forces.

The frequency distribution obtained from the neutron spectra of complex molecules has the greatest validity in the region of lattice modes, since for these modes the molecules move as single entities similar to atoms in a monatomic crystal.

The calculation of C_v vs T has been performed in the case of RDX and β and γ HMX, using the frequency distributions $g(\nu)$, up to 500 cm^{-1}, derived from the time-of-flight data. The low temperature portion of this curve offers the most reliable values of C_v since lattice modes represent the major contribution to C_v in that region. It is unfortunate that in the case of HMX there are no measured values of the specific heat to compare with these results. For RDX, Cp has been measured only in a narrow temperature range (around room temperature). The change in free energy Δ F, internal energy Δ E and entropy Δ S for the transformation β HMX $\longrightarrow$ γ HMX are estimated to be +1 Kcal/mole, +0.144 Kcal/mole and +2.8 entropy units, respectively. The Δ E of this transformation is very small, but this is not unexpected since no bond is broken in the transformation. Only a change in the intermolecular forces takes place, due to different packing and molecular environment. The increase in entropy is going from β to γ HMX suggests that the γ structure is more disordered than the β structure. Neutron diffraction data of β HMX obtained in this laboratory have shown a certain amount of rotational freedom of the CH$_2$ groups in the lattice. These CH$_2$ librational motions (hindered rotations) probably increase in amplitude in the γ structure.

Lead Styphnate, Picric Acid, Styphnic Acid: The study of these three compounds was undertaken because they provide a series having similar molecular structure but vastly different explosive properties. Lead styphnate is one of the most sensitive primary explosives known, comparable to lead azide and nitroglycerin in impact sensitivity. Picric acid is also an explosive but much less sensitive to impact than lead styphnate, while styphnic acid is the most stable. There has been considerable discussion concerning the still unresolved structure of normal lead styphnate. Two structures have been proposed:

Because no large single crystals of normal lead styphnate have thus far, been available, it has not been possible to employ x-ray or neutron diffraction techniques to determine the structure directly. Infrared measurements have been performed in the 600-4000 cm^{-1} frequency range[4] which, because of the absence of a peak in the 3100-3400 cm^{-1} region, have been interpreted to suggest the absence of water of hydration. However, no line corresponding to O-H stretching is observed either so that the results are inconclusive. A NMR study of lead styphnate in H_2O solution also failed to identify the correct structure.[5]

It was hoped that a study of the neutron spectrum of hydrated lead styphnate could give evidence as to whether I or II was the correct structure. The neutron spectrum of lead styphnate is shown in Figure 3. This spectrum is not too different from those obtained from a large number of hydrates. The intense peaks at 430 and 350 cm^{-1} might correspond to a composite of transitions due to H_2O librations and Pb-OH$_2$ stretching and those at 230 and 200 cm^{-1} might be due to hydrogen bond stretching, all of which are observed in other hydrates. Unfortunately, the interpretation of this spectrum is complicated by the presence of low energy intramolecular modes of the styphnate ring.

The spectra of neutrons scattered from styphnic acid and picric acid are shown in Figure 4(a) and 4(b). Because of the similarity of the structure of these three molecules, one might be able to identify the intramolecular vibrations of the ring itself if they are common to all. Table 2 summarizes the neutron scattering data for these three compounds, tentative assignments of the vibrational frequencies and also the available infrared data for the frequency range below 1200 cm^{-1}. In styphnic acid in which no water of hydration exists, a peak is observed at 415 cm^{-1}, while none occurs in picric acid. This mode of vibration may also give rise to the 430 cm^{-1} peak in lead styphnate. Consequently, although the neutron spectrum of normal lead styphnate is very similar to spectra of salts containing water of hydration, the existence of ring deformation frequencies at 430 and 350 cm^{-1} in both the neutron spectra of lead styphnate and styphnic acid seem to favor structure II of lead styphnate.

The general features of the spectra of these three compounds which have greatly different physical properties are of considerable interest. The neutron spectrum of picric acid, a mild explosive, is quite complex, displaying several sharp peaks in the frequency range above 300 cm^{-1} and these are probably due to intramolecular modes. The spectrum of styphnic acid, which is not an explosive, shows a continuous increase in scattered neutron intensity from the region of lattice modes ($\sim$100 cm^{-1}) to that of intramolecular vibrations ($>$ 200 cm^{-1}) with no clear separation. The spectrum of normal lead styphnate which is the most sensitive to impact shows some separation between inter- and intra-molecular modes with intensity considerably lower in the region of intermolecular modes or

lattice vibrations. To quantitatively interpret these differences in terms of differences in inter- and intra-molecular forces, and to relate them to thermodynamic and explosive properties would require a) a calculation of the vibrational frequencies of the isolated molecules and this has been undertaken and b) a detailed knowledge of the crystal structures. However, good single crystals of these materials have not, as yet, been obtained. Finally, the values of C_v as a function of temperature for picric acid and lead styphnate have been calculated from the neutron data. Only values of C_p have been measured and these in a narrow temperature range in the vicinity of $300°K$.

<u>Correlation with Sensitivity</u>: In addition to the assignment of vibrational frequencies in the 0-800 cm^{-1} frequency range an attempt has been made to correlate our microscopic observations with some of the physical properties of the explosives under study.

In a molecular crystal there are not only intramolecular vibrations (within a given molecule) but also intermolecular motions in which adjacent molecules vibrate relative to each other. These intermolecular motions (lattice modes) are generally of lower energy than the intramolecular motions since the forces binding adjacent molecules are weaker than those binding the atoms within the molecule. The probability of thermally exciting a vibration whose energy is ε, is given by

$$P(\varepsilon) = (\exp^{\varepsilon/kt} - 1)^{-1}.$$

An examination of this expression shows that the thermal energy available to a crystal will be primarily deposited in the low frequency vibrations which the crystal can sustain. The amount of energy given to the intramolecular vibrations will therefore depend very strongly upon the relative density of the low energy lattice vibrations. This consideration should be of importance since the molecular vibrations strain those intramolecular bonds whose rupture leads to a release of large amounts of energy. In general, therefore, one would expect that the larger the fraction of available thermal energy which is deposited in intramolecular vibrations, the easier will it be to rupture molecular bonds.
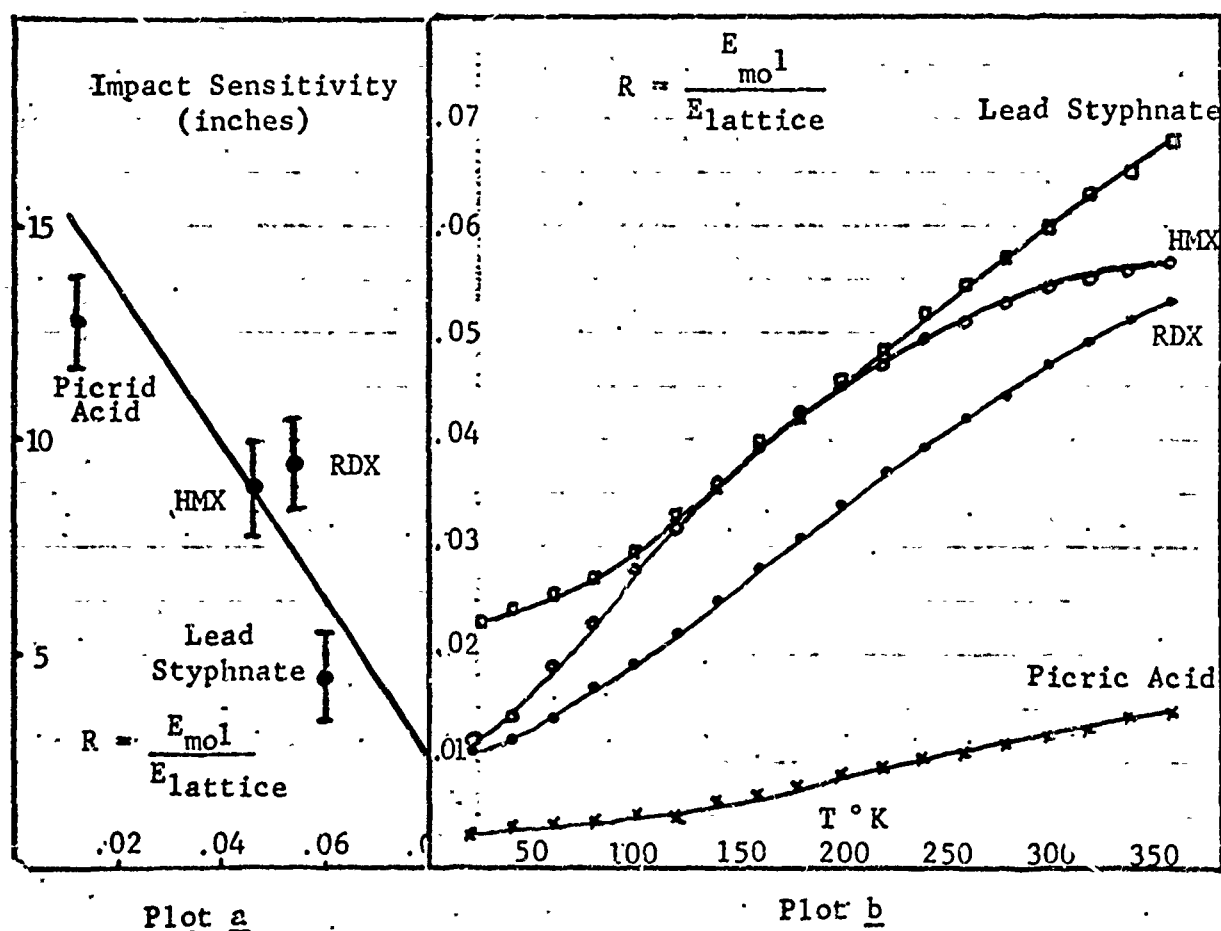
The lattice modes also influence the first mechanism of the growth reaction described earlier, since the probability of formation of a "hot spot" in a localized region of the crystal is dependant upon the ease with which the crystal lattice is able to dissipate thermal energy. This conductivity is determined by the lattice vibrations. Thus lattice modes condition the crystal to promote the formation of "hot spots" which will subsequently lead to explosion.

An attempt has therefore been made to relate the vibrational and physical properties of the compounds under study. The internal energy E (T) has been calculated from the relation

$$E(T) = 3Nr \int_{\varepsilon_1}^{\varepsilon_2} \frac{\varepsilon}{2} \coth \frac{\varepsilon}{kT} g(\varepsilon) \, d\varepsilon$$

where 3Nr is the number of degrees of freedom, $\mathcal{E}$ is the vibrational energy and $g(\mathcal{E})$ is the frequency distribution derived from the neutron data. This expression is rigorously valid in the harmonic approximation only and, as pointed out previously, the applicability of $g(\mathcal{E})$ is limited by various approximations. The ratio R is formed of the internal energy of the low energy intramolecular vibrations (200-800 cm^{-1}) to the internal energy of the lattice modes (0-200 cm^{-1}). The value of this ratio has been plotted in the figure shown below against the measured impact sensitivity for each of the four explosives considered in this work. The impact test value is a minimum height at which at least one of ten trials results in explosion[6]. This value for each material depends upon the test conditions. However, there is general agreement concerning the order in which explosives should be classified.

Plot **a**   Plot **b**

Plot **a** substantiates the qualitative arguments presented above and shows clearly that the explosive becomes more sensitive as R increases. The ratio R was also plotted as a function of temperature (Plot **b**) and according to this calculation, the sensitivity of the four explosives should vary at different rates with temperature. In particular βHMX and picric acid should show the greatest difference in the rate of change near room temperature (βHMX having the slowest rate and picric acid the greatest). Measurements of the temperature dependance of the impact sensitivity of these explosives would constitute a very good test of these calculations.

Finally in the case of explosives where the impact sensitivity is known to vary with the amount of "doping", a study of the corresponding changes in the value of the ratio R with the amount of impurities will be undertaken in order to provide additional evidence substantiating the correlation described in this paper.

CONCLUSION

The inelastic scattering of neutrons provides a means of studying explosives by which the nature of molecular motions can be determined and through which molecular dynamics can be correlated with macroscopic properties such as thermodynamic quantities. A tentative correlation has been made between explosive sensitivity and internal energy for four explosives. These results show the importance of understanding the microscopic behavior in order to predict explosive characteristics.

A number of additional experiments are planned for a more complete understanding of the mechanism of the growth of reactions at the molecular level and to further test the correlation obtained in the present work.

ACKNOWLEDGMENTS

The authors want to thank Drs. P. J. Kemmey and H.J. Matsuguma for stimulating discussions. They are also indebted to Mr. L.H. Eriksen and Dr. J.V.R. Kaufman for their constant interest and support in the course of this work.

REFERENCES

1. Cook, M.A., "Science of High Explosives", Rheinhold, N.Y., 1958.

2. Kemmey, P.J. and Matsuguma, H.J., private communication.

3. Kamenetskii, Frank, Acta Physiochem $\underline{10}$, 365, 1939.

4. Zingaro, R.A., Journal of American Chem. Soc. $\underline{76}$, 816, 1954.

5. Richter, T., private communication.

6. Tomlinson, W.L., Jr., Picatinny Arsenal Technical Report 1740, April 1958.

FIG. I - TIME OF FLIGHT SPECTRA OF NEUTRONS INELASTICALLY SCATTERED BY POLYCRYSTALLINE SAMPLES OF β AND γ HMX. THE NUMBERS CORRESPOND TO FREQUENCY OF VIBRATIONS IN CM^{-1}
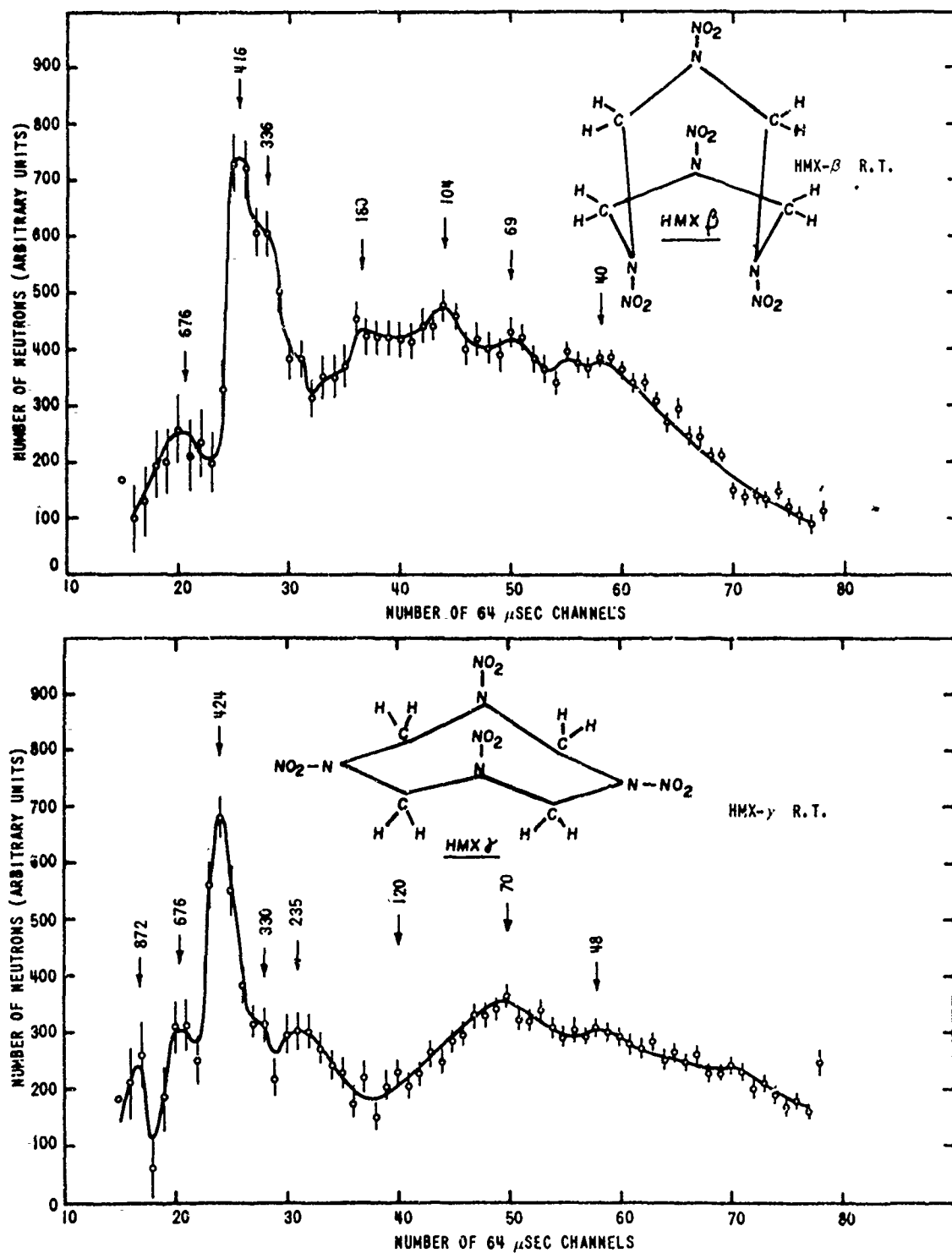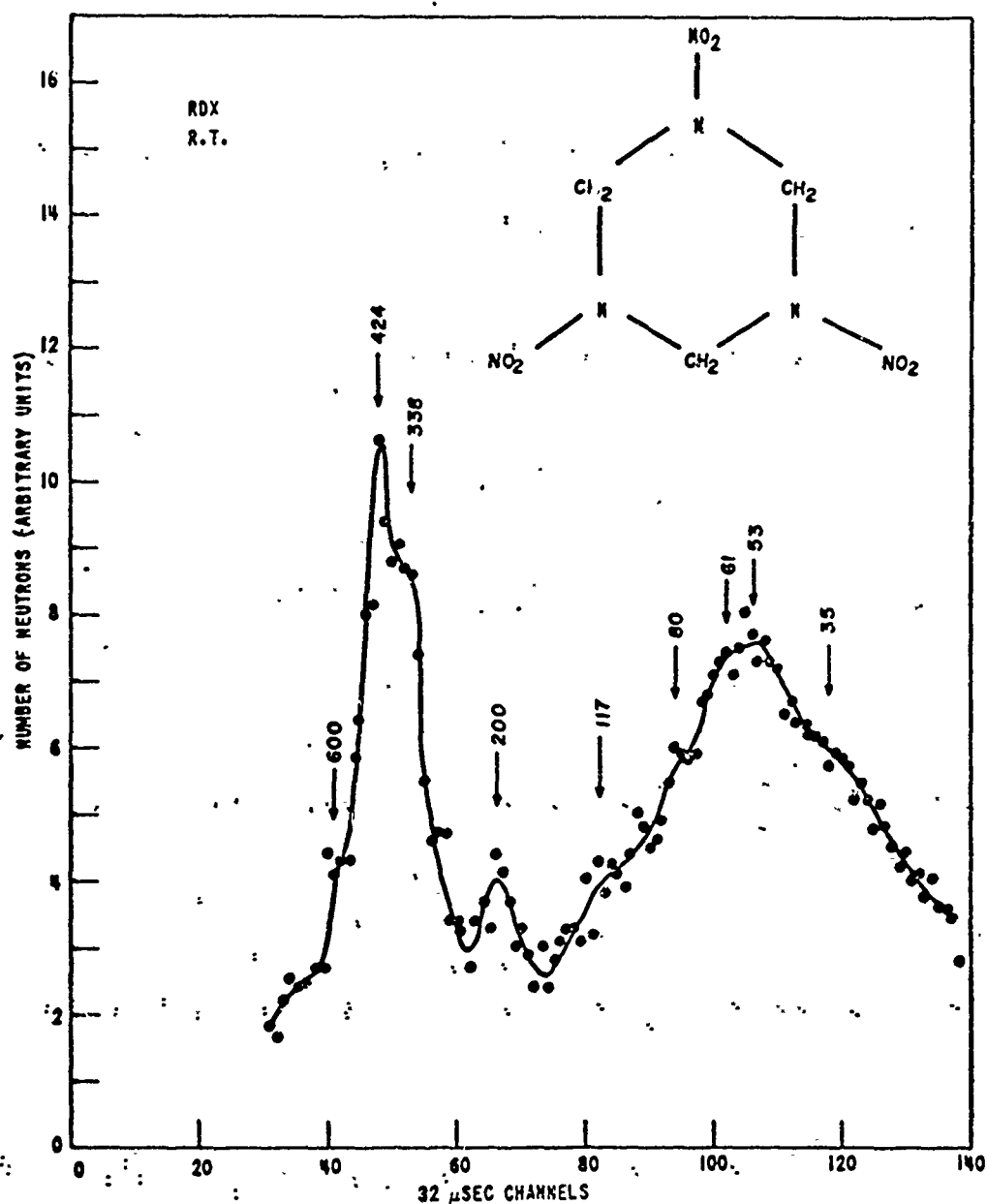
FIG. 2 - TIME OF FLIGHT SPECTRUM OF NEUTRONS INELASTICALLY SCATTERED BY A
POLYCRYSTALLINE SAMPLE OF RDX. THE NUMBERS CORRESPOND TO FREQUENCY
OF VIBRATIONS IN CM⁻¹

BOUTIN, PRASK and TREVINO

Table I

Frequencies of Vibration (0-1200 cm^{-1})

β-HMX Neutron[1]	β-HMX I.R.[2]	γ-HMX Neutron[1]	γ-HMX I.R.[2]	RDX Neutron[1]	RDX I.R.[3]	Assignments
	1202		1280			
			1210			
	1148					
	1090		1088		1035	
			1015		1015	
	968		967			
	949		940			
	919		911			
		b-870		b-890		
	864		862			
	832		840			
	773		764		772	
	762		732		751	
			707		737	
b[4] -670		b-670		600		ring deformation or CH bending
416		424		424		
336		330		338		
180		235		200		NO$_2$ torsions
		120		117		
104				80		
69		70				lattice modes
				55		
40		48		35		

1) This work.

2) Bedard et al., Can. J. Chem. <u>40</u>, 2278 (1962).

3) Myers & Bedard, CARDE Tech Memo 139/57, Jan. 1957
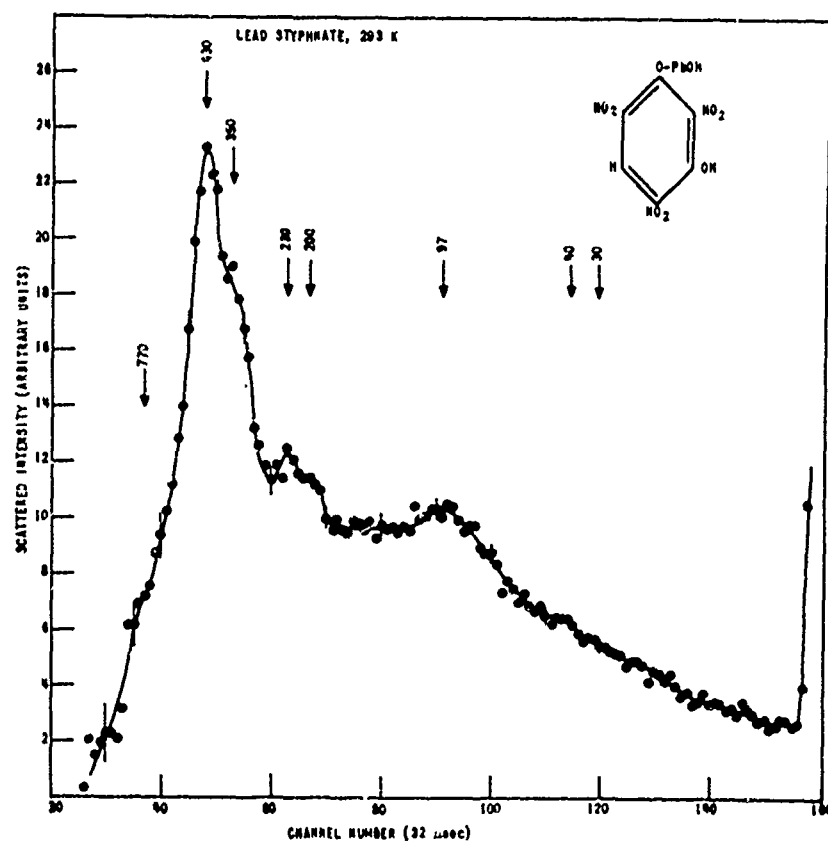
4) Prefix b denotes a broad peak.

FIG. 3 - TIME OF FLIGHT SPECTRUM OF NEUTRONS INELASTICALLY SCATTERED BY A
POLYCRYSTALLINE SAMPLE OF LEAD STYPHNATE. THE NUMBERS CORRESPOND
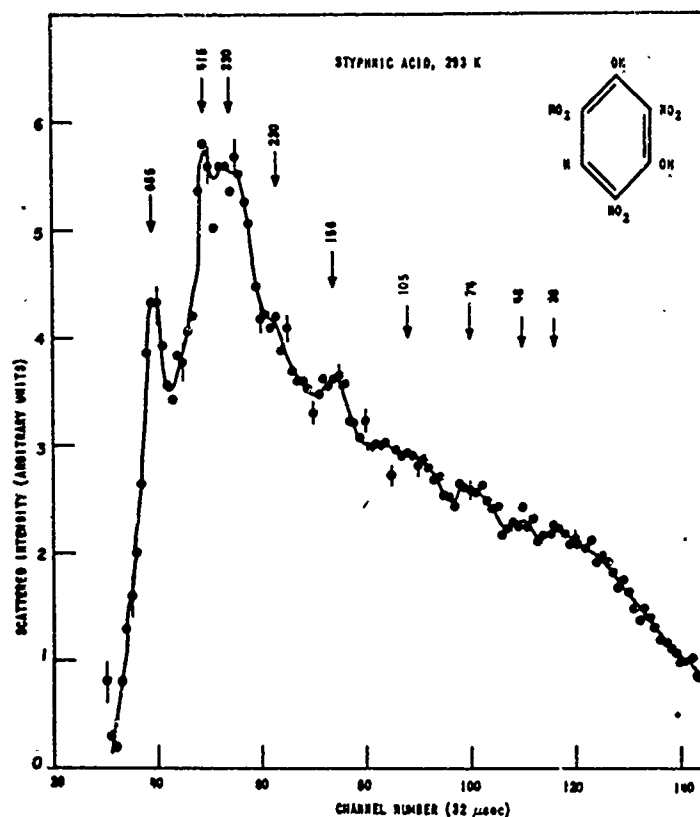TO VIBRATIONAL FREQUENCIES IN CM^{-1}.

FIG. 4(A) TIME OF FLIGHT SPECTRUM OF NEUTRONS INELASTICALLY SCATTERED
BY A POLYCRYSTALLINE SAMPLE OF STYPHNIC ACID. THE NUMBER
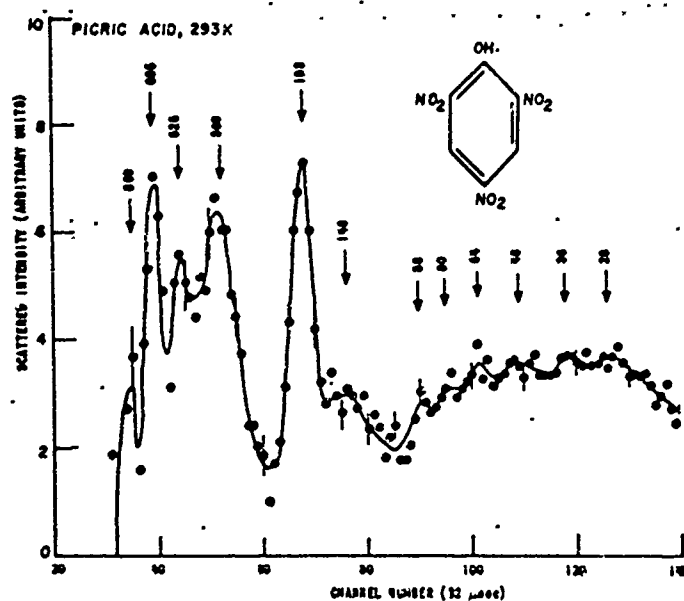CORRESPOND TO FREQUENCY OF VIBRATIONS IN CM⁻¹

FIG. 4(B) TIME OF FLIGHT SPECTRUM OF NEUTRONS INELASTICALLY SCAT-
TERED BY A POLYCRYSTALLINE SAMPLE OF PICRIC ACID. THE
NUMBERS CORRESPOND TO VIBRATIONAL FREQUENCIES IN CM⁻¹

Table II

Frequencies of Vibration (0-1200 cm^{-1})

Pb Styphnate		Styphnic Acid		Picric Acid		Assignment
Neutron[1]	I.R.[2]	Neutron[1]	I.R.[3]	Neutron[1]	I.R.[3]	
	1180					
	1130		1080		1080	
	1100					
	1080					
	980		930		940	
	940				915	
				860		
			772		775	
			755		735	
	730		775		720	
b[5] -770			718		705	
	690	685	690	685		ring defor-
				525		mation or CH
430	415					bending
350	330			360		
230	230					
200				193		
		156		148		
97		b-105				
				88		
		74		80	broad band	lattice modes
				64		
40		48		48		
				36		
30		38		28		

1) This work.

2) R. Zingaro, J. Amer. Chem. Soc. 76, 816 (1954).

3) F. Pistera et al., Anal. Chem. 32, 495 (1960).

4) Prefix b denotes a broad peak.